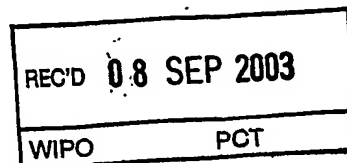


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Polymerisation catalyst

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### **POLYMERISATION CATALYST**

The present invention relates to the preparation of polymerisation catalysts, and in particular to the preparation of silica containing metallocene catalyst components for use in the polymerisation of olefins.

In recent years there have been many advances in the production of polyolefin homopolymers and copolymers due to the introduction of metallocene catalysts. Metallocene catalysts offer the advantage of generally a higher activity than traditional Ziegler catalysts and are usually described as catalysts which are single site in nature.

There have been developed several different families of metallocene complexes. In earlier years catalysts based on bis (cyclopentadienyl) metal complexes were developed, examples of which may be found in EP 129368 or EP 206794. More recently complexes having a single or mono cyclopentadienyl ring have been developed. Such complexes have been referred to as 'constrained geometry' complexes and examples of these complexes may be found in EP 416815 or EP 420436. In both of these complexes the metal atom eg. zirconium is in the highest oxidation state.

Other complexes however have been developed in which the metal atom may be in a reduced oxidation state. Examples of both the bis (cyclopentadienyl) and mono (cyclopentadienyl) complexes have been described in WO 96/04290 and WO 95/00526 respectively.

The above metallocene complexes are utilised for polymerisation in the presence of a cocatalyst or activator. Typically activators are aluminoxanes, in particular methyl aluminoxane or compounds based on boron compounds. Examples of the latter are borates such as trialkyl-substituted ammonium tetraphenyl- or tetrafluorophenyl-

borates. Catalyst systems incorporating such borate activators are described in EP 561479, EP 418044 and EP 551277.

The above metallocene complexes may be used for the polymerisation of olefins in solution, slurry or gas phase. When used in the gas phase the metallocene complex and/or the activator are suitably supported. Typical supports include inorganic oxides eg. silica or polymeric supports may alternatively be used.

Examples of the preparation of supported metallocene catalysts for the polymerisation of olefins may be found in WO 94/26793, WO 95/07939, WO 96/00245, WO 96/04318, WO 97/02297 and EP 642536.

Supported metallocene catalysts may be prepared by use of sol-gel techniques.

Silicate gels are typically prepared by hydrolyzing monomeric tetrafunctional alkoxide precursors utilizing a mineral acid or base as a catalyst. For example the hydrolysis and condensation of tetraethoxysilane in a sol-gel process catalysed by ammonia results in a sol-gel powder which may be used as an organometallic catalyst support.

In *J. Applied Polymer Science Vol. 78, 2318 – 2326 (2000)* there is described silica supports for metallocenes prepared by the gelation of a stable colloidal phase of silica using  $MgCl_2$  as initiator. *Polymer Bulletin 46, 175 – 182 (2001)* describes the synthesis of metallocene catalysts supported on silica type sol-gel carriers. The silica gels were prepared in a wet sol-gel procedure by hydrolysis and condensation of tetraethoxysilane in a mixture of water, ethyl alcohol and ammonia. *Polymer 42, 2001 pgs 4517 – 4525* describes the preparation of supported metallocenes by use of xerogels based on the hydrolysis and condensation reactions between tetraethoxysilane and bis(indenyl)diethoxysilane. In all the above preparations the resultant supported catalysts were employed in the polymerisation of ethylene.

We have now surprisingly found that sol-gel techniques which utilise a non-hydrolytic procedure may be successfully used in the preparation of silica containing metallocene catalyst components for the polymerisation of olefins.

Thus according to the present invention there is provided a process for the preparation of a silicon containing metallocene catalyst component, said process comprising the steps of

- (a) non-hydrolytic sol-gel condensation of a (cyclopentadienyl)

dihalogenated silane with an halogenated silane (or siloxane) and an alkoxy silane,

- (b) alkylation
- (c) deprotonation and
- (d) addition of a Group IVA metal compound.

5

The (cyclopentadienyl) dihalogenated silane is typically a dichlorinated compound.

- 10 The preferred silanes are those having one or two cyclopentadienyl ligands however bis(cyclopentadienyl) compounds for example bis(cyclopentadienyl)dichlorosilanes or bis(indenyl)dichlorosilanes are most preferred.

The preferred alkoxy silanes are ethoxy silanes for example tetraethoxy silane.

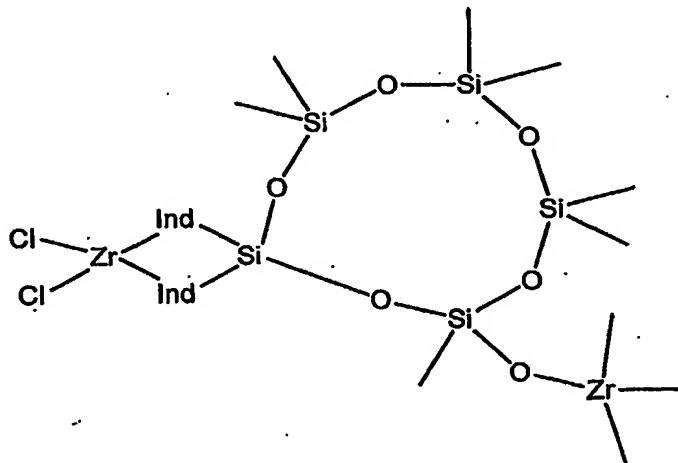
The preferred halogenated silanes are chlorosilanes for example tetrachlorosilane or dimethyldichlorosilane.

- 15 The alkylation step may be carried out by use of well known passivation agents, for example triethylaluminium.

The deprotonation step may be carried out by use of well known deprotonation agents for example n-butyllithium.

- 20 The Group IVA metal compound may typically contain zirconium, titanium or hafnium metal and is preferably a halogenated compound. Preferred compounds are zirconium tetrachloride or titanium tetrachloride.

The silicon containing metallocene catalyst component prepared according to the process of the present invention may typically have the following structure:



The metallocene catalyst component may be used for the polymerisation of olefins in the presence of any suitable activator component well known for use with metallocene catalysts.

5 Preferred activator components are aluminoxanes for example methyl aluminoxane (MAO).

Other activator components include boron compounds for example boranes such as tris(pentafluorophenyl) borane or borates such as tributyl ammonium tetrephenylborate.

10 The metallocene components of the present invention may be used for the polymerisation of olefins in either the solution, slurry or gas phase.

The metallocene components are most suitable for operation in the gas phase. Gas phase processes for the polymerisation of olefins, especially for the homopolymerisation and the copolymerisation of ethylene and  $\alpha$ -olefins for example 1-butene, 1-hexene, 4-methyl-1-pentene are well known in the art.  
15 Particularly preferred gas phase processes are those operating in a fluidised bed. Examples of such processes are described in EP 89691 and EP 699213 the latter being a particularly preferred process for use with the supported catalysts of the present invention.

Particularly preferred polymerisation processes are those comprising the  
20 polymerisation of ethylene or the copolymerisation of ethylene and  $\alpha$ -olefins having from 3 to 10 carbon atoms.

In another embodiment of the present invention silicon containing metallocene catalyst components may suitably be prepared by the following steps:

- 25 (a) non-hydrolytic sol-gel condensation of a (cyclopentadienyl) dihalogenated silane with an halogenated silane (or siloxane) and an alkoxysilane,  
(b) alkylation, and  
(c) addition of a Group IVA metal compound.

Suitable halogenated siloxanes for step (a) include for example  
30 dichlorotetramethylsiloxanes.

Suitable Group IV metal compounds for this embodiment of the present invention include metal amides for example  $Zr(NMe)_4$  or similar.

This aspect of the present invention may additionally include a final step for example addition of chlorotrimethylsilane thereby forming the metal dichloride species.

The process according to this aspect of the present invention may be illustrated with reference to the accompanying Figure which shows the reaction scheme for the preparation of supported catalyst components based on bis(indenyl) dichlorosilane.

The present invention will be further described by reference to the following examples:

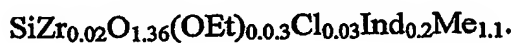
#### Example 1

##### 10 Preparation of support No:1

In a glove box, zirconium tetrachloride (0.18 mmol) and bis(indenyl)dichlorosilane\* (1.01 mmol) were introduced into a Schlenk tube. The tube was connected to a vacuum/N<sub>2</sub> line and dimethyldichlorosilane (4.51 mmol) and tetraethoxysilane (2.83 mmol) were successively added via syringes. The mixture was stirred for 5 minutes and transferred via a syringe to another tube which was then sealed under vacuum. The sealed tube was introduced in a steel envelope and held in an oven at 110 – 115°C. After 8 days the tube was opened in a glove box under N<sub>2</sub> and the resultant gel dried under vacuum at room temperature for 6 hrs. The chemical composition of the gel was as follows:

Elemental Analysis	C	H	Cl	Si	Zr	O
Mass %	31.96	5.34	2.36	30.75	1.4	28.19

These results indicate a final structure of :



NB. \* prepared according to Organometallics 1993, 12, 4607-4612.

#### Example 2.

##### 25 Preparation of Metallocene catalyst component A

1.94 mmol of n-butyl lithium was added dropwise at room temperature to 163 mg. of Support No: 1, prepared in example 1, in suspension of pentane (nBuLi/Indenyl = 5.5). The reaction mixture was kept under reflux for 7 hrs. The solvent was removed under vacuum and the solid washed with 3 aliquots of 8 ml. pentane and then dried under vacuum at room temperature for 1 hr.

To the suspension of the resulting solid in 10 ml tetrahydrofuran, 0.177 mmol  $\text{ZrCl}_4 \cdot 2\text{THF}$  in tetrahydrofuran were added dropwise at room temperature. The mixture was then stirred for 1 hr. The resultant solid was then filtered, washed with 2 aliquots of 10 ml. tetrahydrofuran and dried under vacuum.

### 5 Example 3

#### Polymerisation of component A

In a Schlenk tube were introduced 6.8 mg. of the metallocene catalyst component A, prepared in example 2, ( $6.3 \mu\text{mol Ind}_2\text{ZrCl}_2$ ), 50 ml toluene and 4.2 ml of methyl aluminoxane ( $\text{Al/Zr} = 1000$ ). After stirring for 10 min. the system was  
10 degassed. The mixture was held at  $60^\circ\text{C}$  and a continuous flow of ethylene (pressure = 1 bar) was maintained. After 1 hr. the polymerisation was terminated by adding acidic ethanol. The precipitated polymer was filtered and dried under vacuum for 8 hr. at room temperature. 1.01 g. of polyethylene was obtained corresponding to an activity of 110  $\text{gPE}/(\text{g}_{\text{catalyst}} \cdot \text{h} \cdot \text{bar})$ .

15 The polymer was characterised as having  $M_n = 44800$ ,  $M_w = 124100$  and  $MWD = 2.8$ .

### Example 4

#### Preparation of support No: 2

In a glove box, zirconium tetrachloride (0.352 mmol) and  
20 bis(indenyl)dichlorosilane\* (3.01 mmol) were introduced into a Schlenk tube. The tube was connected to a vacuum/ $\text{N}_2$ -line and dichlorotetramethylsiloxane (5.093 mmol) and tetraethoxysilane (4.403 mmol) were successively added via syringes. The mixture was stirred for 5 minutes and transferred via a syringe to another tube which was then sealed under vacuum. The sealed tube was introduced in a steel envelope and held in an oven  
25 at  $110 - 115^\circ\text{C}$ . After 8 days the tube was opened in a glove box under  $\text{N}_2$  and the resultant gel dried under vacuum at room temperature for 6 hrs. The chemical composition of the gel was as follows:

Elemental Analysis	C	H	Cl	Si	Zr	O
Mass %	44.71	5.79	5.35	24.75	1.61	17.79

These results indicate a final structure of :

30  $\text{SiZr}_{0.02}\text{O}_{1.12}(\text{OEt})_{0.11}\text{Cl}_{0.11}\text{Ind}_{0.34}\text{Me}_{1.16}$ .



NB. \* prepared according to Organometallics 1993, 12, 4607-4612.

#### Example 5.

##### Preparation of Metallocene catalyst component B

5 A suspension of Support No:2 (120mg corresponding to 1.12mmol of Si) in pentane was reacted with TEA (0.67 mmol). The mixture was kept stirring for 6 hours. After stopping the stirring and waiting for the decantation, the supernatant liquid was removed by the use of a canula. The resulting solid was washed with pentane in the same manner and dried under vacuum.

10 1.91 mmol of n-butyl lithium was added dropwise at room temperature to a suspension of the passivated solid in pentane ( $n\text{BuLi/Indenyl} = 5$ ). The reaction mixture was kept under reflux overnight. After stopping the stirring and waiting for the decantation, the supernatant liquid was removed by the use of a canula. The solid was washed with pentane in the same manner and dried under vacuum.

15 To the suspension of the resulting solid in tetrahydrofuran, 0.191 mmol  $\text{ZrCl}_4 \cdot 2\text{THF}$  in tetrahydrofuran were added dropwise at room temperature. The mixture was then stirred for 1 hr. The solvent was eliminated by vacuum, pentane was added, the suspension was kept stirring for 1h. After stopping the stirring and waiting for the decantation, the supernatant liquid was removed by the use of a canula. The solid was dried under vacuum.

#### 20 Example 6

##### Polymerisation of component B

25 In a Schlenk tube were introduced 3.9 mg of the metallocene catalyst component A, prepared in example 5, ( $4.9 \mu\text{mol Ind}_2\text{ZrCl}_2$ ), 50 ml toluene and 3.2 ml of methyl aluminoxane ( $\text{Al/Zr} = 1000$ ). After stirring for 10 min. the system was degassed. The mixture was held at  $60^\circ\text{C}$  and a continuous flow of ethylene (pressure = 1 bar) was maintained. After 1 hr. the polymerisation was terminated by adding acidic ethanol. The precipitated polymer was filtered and dried under vacuum for 8 hr. at room temperature. 0.74 g. of polyethylene was obtained corresponding to an activity of 190  $\text{gPE}/(\text{g}_{\text{catalyst}} \cdot \text{h} \cdot \text{bar})$ .

30 The polymer was characterised as having  $M_n = 8700$ ,  $M_w = 168400$  and  $MWD = 19$ .

#### Example 7

### Preparation of support No:3

In a glove box, zirconium tetrachloride (0.417 mmol) and bis(indenyl)dichlorosilane\* (2.1 mmol) were introduced into a Schlenk tube. The tube was connected to a vacuum/N<sub>2</sub> line and dichlorotetramethylsiloxane (6.913 mmol) and tetraethoxysilane (4.923 mmol) were successively added via syringes. The mixture was stirred for 5 minutes and transferred via a syringe to another tube which was then sealed under vacuum. The sealed tube was introduced in a steel envelope and held in an oven at 110 – 115°C. After 11 days the tube was opened in a glove box under N<sub>2</sub> and the resultant gel dried under vacuum at room temperature for 6 hrs. The chemical

composition of the gel was as follows:

Elemental Analysis	C	H	Cl
Mass %	39.28	6.00	3.97

These results indicate a final structure of :



NB. \* prepared according to Organometallics 1993, 12, 4607-4612.

### 15 Example 8

#### Preparation of Metallocene catalyst component C

A suspension of Support No:3 (145.4 mg corresponding to 1.58 mmol of Si) in pentane was reacted with TEA (0.98 mmol). The mixture was kept stirring for 20 hours. After stopping the stirring and waiting for the decantation, the supernatant liquid was removed by the use of a canula. The resulting solid was washed with pentane in the same manner and dried under vacuum.

0.16 mmol of Zr(NMe<sub>2</sub>)<sub>4</sub> was added at room temperature to support No. 3 (Zr(NMe<sub>2</sub>)<sub>4</sub>/Indenyl = 0.5). Toluene was added and the reaction was stirred overnight at 100°C. The solvent was removed via reduced pressure. Pentane and chlorotrimethylsilane (3.2 mmol) were then added and the reaction was stirred overnight at room temperature. After stopping the stirring and waiting for the decantation, the supernatant liquid was removed by the use of a canula. The solid was washed with THF and pentane in the same manner and dried under vacuum.

### 30 Example 9

### Polymerisation of component C

In a Schlenk tube were introduced 6 mg. of the metallocene catalyst component C (corresponding to a theoretical amount of  $5.5 \mu\text{mol Ind}_2\text{ZrCl}_2$ ), 50 ml toluene and methyl aluminoxane ( $\text{Al/Zr} = 1000$ ). After stirring for 10 min. the system was  
5 degassed. The mixture was held at  $60^\circ\text{C}$  and a continuous flow of ethylene (pressure = 1 bar) was maintained. After 1 hr. the polymerisation was terminated by adding acidic ethanol. The precipitated polymer was filtered and dried under vacuum for 8 hr. at room temperature. 0.327 g. of polyethylene was obtained corresponding to an activity of 65 gPE/(g<sub>catalyst</sub>·h·bar).

10 The polymer was characterised as having  $M_w = 317 \text{ kg/mol}$  and  $MWD = 45$ .

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**Claims:**

1. A process for the preparation of a silicon containing metallocene catalyst component, said process comprising the steps of

(a) non-hydrolytic sol-gel condensation of a (cyclopentadienyl) dihalogenated silane with an halogenated silane (or siloxane) and an alkoxysilane,

5 (b) alkylation,

(c) deprotonation, and

(d) addition of a Group IVA metal compound.

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**ABSTRACT**  
**POLYMERISATION CATALYST**

A process for the preparation of a silicon containing metallocene catalyst component comprises the steps of

- (a) non-hydrolytic sol-gel condensation of a (cyclopentadienyl) dihalogenated silane with an halogenated silane (or siloxane) and an alkoxysilane,
- (b) alkylation,
- (c) deprotonation, and
- (d) addition of a Group IVA metal compound.

The novel method allows for the preparation of metallocene catalyst which may suitably be used with activators for the polymerisation of olefins, in particular for such processes carried out in the gas phase.

FIGURE 1

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